Analysis of quasielastic light scattering in LiNbO$_3$ near T_C

Y. Okamoto,* Ping-chu Wang,† and J. F. Scott

Condensed Matter Laboratory, Department of Physics, University of Colorado, Boulder, Colorado 80309-0390

(Received 18 June 1985)

We have performed Raman studies of lithium niobate from 293 to 1224 K with special emphasis upon quantitative analysis of the quasielastic scattering from 0—50 cm^{-1}. We find that the complete spectrum, including both the quasielastic "wing" and the two lowest-frequency A_1-symmetry optical phonons, can be fitted to the spectral distribution function predicted for a system with a relaxing self-energy; when this is done all the parameters fitted vary slowly and monotonically with temperature. The coupling parameter $\delta^2(T)$ varies approximately as $(T_C-T)^{-1.4}$ in accord with the predictions of Halperin and Varma [Phys. Rev. B **14**, 4030 (1976)]. This is only the second central-mode study to satisfy that defect-theory prediction. Both congruent and stoichiometric specimens were examined. The congruent sample exhibits an inverse relaxation time of 540±30 GHz that is independent of temperature; it is apparently limited by defects arising from the lack of stoichiometry. The stoichiometric sample exhibits a temperature-dependent relaxation time of the form $\tau^{-1}(T) = \tau_0^{-1}[(T_C-T)/T_C]$ with $\tau_0^{-1} = 1740 \pm 430$ GHz (i.e., $\tau_0^{-1} = 58 \pm 14$ cm^{-1}); this is the expected mean-field dependence for a second-order phase transition. The data show why inelastic neutron scattering studies [e.g., M. R. Chowdhury, G. E. Peckham, and D. H. Saunderson, J. Phys. C **11**, 1671 (1978)] may have been unable to detect the softening of the lowest A_1-symmetry optical phonon and thereby help resolve a long-standing controversy concerning the qualitative disagreement of Raman and neutron scattering data.

I. INTRODUCTION

The lattice dynamics relating to the ferroelectric phase transitions in LiNbO$_3$ and LiTaO$_3$ have long been a source of controversy. Johnston and Kaminow found[1] that each transition was characterized by "a particular vibrational mode (which) approaches zero frequency in the neighborhood of the transition," and thereby equate these compounds with other displacive ferroelectrics, commenting that "such soft-mode behavior is similar to that found in other experiments" on other materials. In total contradistinction, Chowdhury et al.[2] found in a subsequent inelastic neutron scattering experiment that the phase transition in LiNbO$_3$ is completely order-disorder, with no soft-mode or displacive character. They relate their observations to the case of LiTaO$_3$, where the mixed displacive—order-disorder character of ferroelectricity and the ferroelectric phase transition is much clearer; based primarily upon the work of Abrahams and co-workers[3] and of Lines,[4] it appears that the Li ions in LiTaO$_3$ undergo an order-disorder transition, whereas the behavior of the Ta ions is more nearly displacive.

The intention of the present study consists of several parts: First, we wish to fit quantitatively the quasielastic portion of the light scattering spectrum from zero frequency to the frequency of the lowest optical phonon of A_1 symmetry; such quasielastic scattering was first reported qualitatively in Ref. 1. Second, we want to examine both stoichiometric and congruent specimens to see if they exhibit different spectral responses. LiNbO$_3$ is normally grown as large single crystals pulled from a congruent melt; unfortunately, spectroscopists using these samples[5] do not always understand that their specimens are not stoichiometric and draw erroneous conclusions concerning the order-disorder characteristics apparent in their spectra near T_C (samples 1% off stoichiometry have on the order of 10^{21} "defects"/cm^3 and cannot be expected to exhibit the phenomena characteristic of intrinsic crystals near a phase-transition point). Third, we want to reconcile the apparently unreconcilable results of Refs. 1 and 2 as to the existence of a "soft" optical phonon at $q = 0$ and to the displacive or order-disorder nature of the phase transition.

II. THEORY

The theory we employ to analyze our data is that of a damped harmonic oscillator coupled with an interaction strength δ^2 to some unspecified, phenomenological internal mode that has a Debye relaxation time τ.[6-8] The response function then has the form

$$\chi_0^{-1}(q,\omega,T) = \omega_0^2(q,T) - \omega^2 - i\omega\gamma_0(T) - \frac{\delta^2(T)}{1-i\omega\tau(T)} \qquad (1)$$

and the Raman spectra will be proportional to $kT/\hbar\omega$ times Im$[\chi_0(q,\omega,T)]$. Our fitting procedure is to start with ambient-temperature data (far from T_C) for which ω_0 and γ_0 are easily fitted as approximating the peak position and width of the low-frequency A_1-symmetry optical phonon. As temperature increases, these and the other parameters in Eq. (1) vary slowly, and the fitted parameters at one temperature can be employed as starting values for the least-squares routine at the next higher temperature. By 700 K the quasielastic scattering from 0—50 cm^{-1} is sufficiently strong that reliable values of δ^2 and τ

can be obtained; δ^2 is sufficiently weak at this temperature, however, that the correlation between fitted parameters is still small. Even at the highest temperatures we studied (~ 1200 K), the correlation between γ_0, δ^2, and τ was not large in the fitting procedure. Therefore, we believe that the results to be presented in the following sections involve numerically meaningful parameters.

III. EXPERIMENT

The data used here were all obtained with kyrpton-ion laser excitation at 530.9 nm at power levels on the order of 100 mW. The samples were placed in a wire-wound alumina furnace with quartz windows. Sample temperature could be controlled to ± 1 K over the time required for a spectrum (on the order of 20 min) at 1200 K. The spectral resolution employed for most data runs was 3 cm^{-1}.

Two specimens were used. Both were large rectangular parallelepipeds, x-ray oriented and mechanically polished. Repolishing of the surfaces was necessary after cycling to temperatures above 1000 K. The first specimen was pulled from a congruent melt; it was grown in Nanjing, China. The second specimen was grown at Bell Telephone Laboratories and specified as exactly 1:1 Li-Nb stoichiometry.

Figure 1 shows the spectrum obtained for the congruent specimen at 297 K from 0—500 cm^{-1} for the α_{zz} polarizability tensor. The spectrum is noteworthy in two respects: First, it does not show any "leakthrough" of E-symmetry modes. Such modes were a problem in Ref. 1; their presence in the zz spectra of Ref. 1 was attributed to internal strain in the sample used. Thus, Fig. 1 shows that our specimen was considerably more strain free than that employed by Johnston and Kaminow. The second point to emphasize from this figure is that there are two closely spaced A_1-symmetry modes: These are both A_1 transverse modes, and their frequencies are ~ 250 and 274

cm^{-1}. The A_1 longitudinal branch at ~ 270 cm^{-1} is forbidden for this geometry. It is important in this regard to note that in the inelastic neutron scattering study of Ref. 2 only one mode (at ~ 260 cm^{-1}) was observed of the three[1] well-known A_1 TO, LO, and TO modes at 250, 270, and 274 cm^{-1}, respectively. It seems clear that the authors of Ref. 2 were never able to measure most of the A_1 excitations even at room temperature; they indicate a possible reason for this in their own paper: "The neutron measurements for the A_1 modes were made in a longitudinal position, and hence close to $\cdots$ the zone center one would expect the measured (spectra) to be weighted strongly toward the longitudinal mode." Since the authors of Ref. 2 never measured the lower A_1 TO modes, any speculation they may have about the temperature dependences or lack thereof of these modes is therefore unfounded. We show in the section that follows that these modes are indeed "soft." Before leaving Fig. 1, however, let us note that the solid curve through the data points (circles) is a least-squares fit to $kT/\hbar\omega$ times the imaginary part of the susceptibility given in Eq. (1). (At these temperatures the Bose factor is approximately $kT/\hbar\omega$.) In agreement with Ref. 1, we find that the higher-frequency mode (at 274 cm^{-1}) of the doublet shown is the soft ferroelectric mode. As the temperature increases, this mode will decrease in frequency and move through the lower mode at 239 cm^{-1}. The spectra of the two modes show none of the line-shape anomalies familiar in studies of strongly coupled modes,[9] and so we treat these two modes as uncoupled in the analysis which follows. That is, we add to the susceptibility fitted an extra term

$$\chi_1(q,\omega,T) = [\omega_1^2(q,T) - \omega^2 - i\omega\gamma_1(T)]^{-1} , \qquad (2)$$

but we ignore any direct interaction between modes 0 and 1.

Figure 2 is a superposition of data at different temperatures for this congruent sample. In each case the solid curve is the least-squares fit to the susceptibility, and the arrow marks the position of the "soft mode." We remark that in all these spectra the elastically scattered "laserline" light near $\omega = 0$ was negligible. Our samples were of gemlike quality, and at 3 cm^{-1} or more from $\omega = 0$ such elastic scattering was less than 5% of the inelastic scattering at all temperatures of interest. For this reason 514.5-nm excitation with an iodine absorber was unnecessary.

The parameters obtained from fitting the data shown in Fig. 2 are tabulated in Table I and plotted versus temperature in Fig. 3. It can be seen from Fig. 3 that, although there is a soft mode with a peak frequency that decreases to 100 cm^{-1} or below before it becomes too heavily damped to be distinguished from the quasielastic scattering, the apparent decrease in the peak frequency is almost entirely due to the rapid increase in its linewidth γ_0; its quasiharmonic frequency ω_0 remains nearly independent of T, decreasing only about 10%—the same as mode ω_1—an effect due simply to thermal expansion. Note that the soft mode becomes overdamped at approximately 1100 K. γ_0 varies as $\gamma_0 = (6 \text{ cm}^{-1})e^{kT/\hbar\omega_A}$ with $\omega_A \approx 204$ cm^{-1}. This is *not* the form expected for anharmonic re-
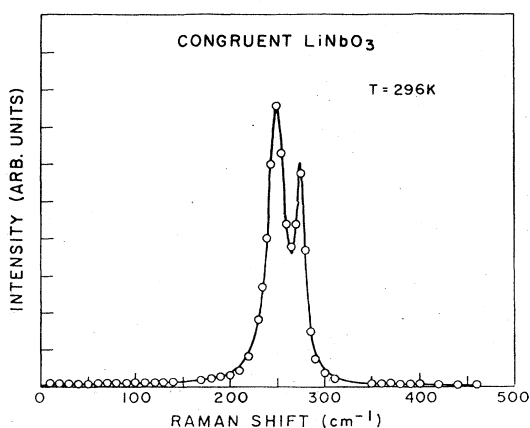

FIG. 1. Raman spectra at 296 K for zz polarizability in congruent LiNbO$_3$, showing the two lowest-frequency A_1(TO) modes at approximately 239 and 274 cm^{-1}. The solid curve is a fit to the function $n(\omega,T)\text{Im}[\chi(\omega,T)]$, using an additive χ consisting of Eqs. (1) and (2).
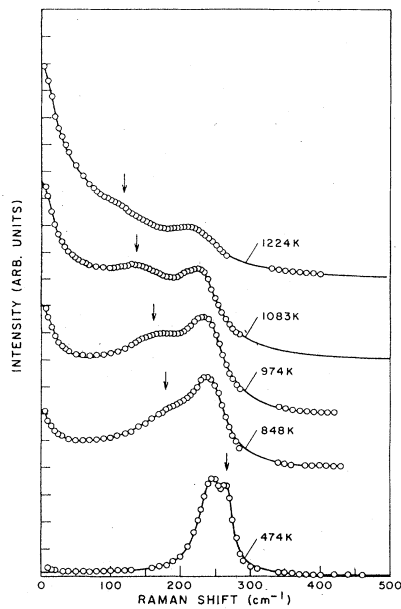
FIG. 2. Raman spectra of congruent LiNbO$_3$, as in Fig. 1. The five traces are, top to bottom taken at 1224, 1083, 974, 848, and 474 K. The arrow on each trace is an aid to the eye and marks the position of the soft-mode peak frequency. The quasielastic scattering in these traces increases in intensity as T is increased toward T_C, but within experimental error its width is independent of T, with a width at half maximum of 18 ± 2 cm^{-1} after the phonon scattering is deconvoluted out.

normalization of a soft mode dominated by decay into other phonons on the same soft branch [see Fig. 3(c)]. Divergent soft-mode linewidths such as these have been studied earlier[10] in PbTiO$_3$ and NdAlO$_3$. The particular empirical algebraic form for $\gamma(T)$ used in Ref. 10 does not work as well for our data, but data are needed above 1300 K for a real test.

In Fig. 3(b) we graph the relaxation parameter τ versus temperature for the congruent-sample data displayed in Fig. 2. Within experimental fitting uncertainty the inverse relaxation time is completely independent of temperature and equals 18 ± 1 cm^{-1}. This temperature-independent result suggests that the high "defect" density due to lack of stoichiometry is dominant. Also shown in Fig. 3(b) is the value of the coupling parameter $\tau\delta^2$ at each temperature; this parameter increases monotonically and supralinearly as T approaches $T_C = 1483\pm10$ K from below. The maximum value of $\tau\delta^2$ we measure (at 1224 K) is 1434 cm^{-1}. As an approximation,[8] the scattering intensity within the quasielastic wing compared with that under the damped soft mode should equal δ^2/ω_0^2 at each temperature at which the two components can be resolved. Testing this relationship in our data gives, for example, at $T = 974$ K, where $\omega_0(T) = 220$ cm^{-1} and $\delta = 91$ cm^{-1}, the prediction that 17% of the intensity should lie in the central mode. The experimental value is very close: $17\pm3\%$.
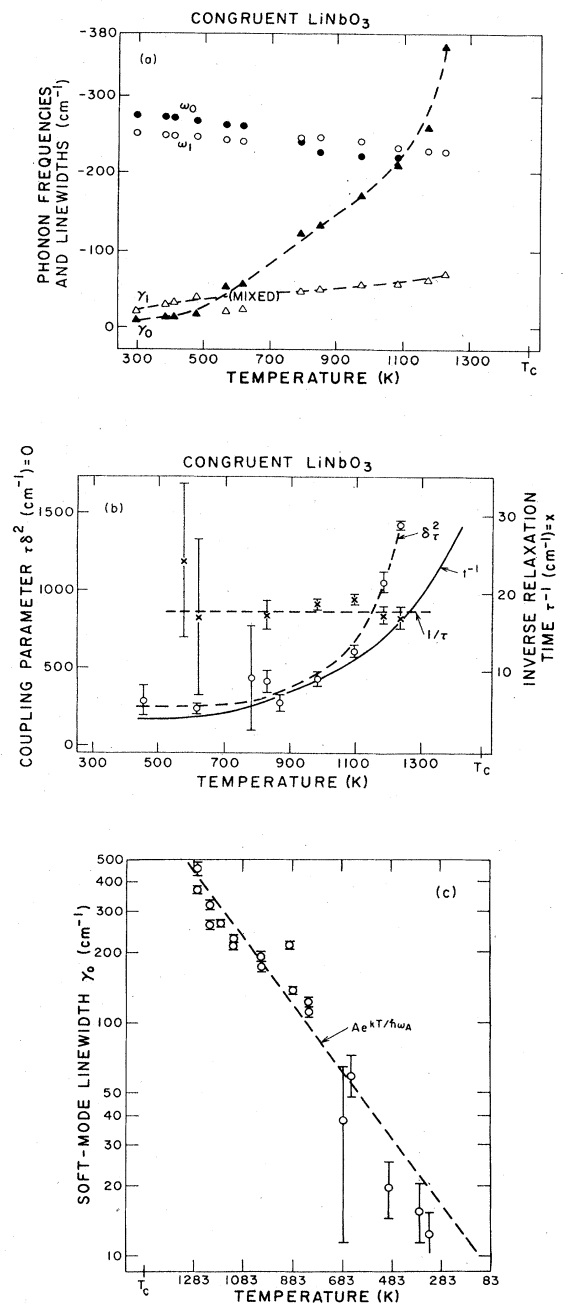
FIG. 3. (a) Temperature dependences of the fitting parameters for the spectra in Fig. 2. ω_0 and ω_1 are the quasiharmonic frequencies of the two lowest-energy A_1(TO) phonons in congruent LiNbO$_3$; γ_0 and γ_1, their linewidths. (b) Temperature dependences of the relaxation parameters for the spectra in Fig. 2. All error bars are one standard error. δ^2 is the constant which describes coupling between the soft optic phonon and a phenomenlogical Debye relaxation, and $1/\tau$ is the inverse of the relaxation time of the latter. This congruent sample shows, within experimental uncertainty, no temperature dependence of its relaxation time, but δ^2 varies as $(T_C - T)^{-1}$ (solid curve). (c) Linewidth γ_0 for the soft mode. This semilog plot of γ_0 versus temperature shows that γ_0 is proportional to $e^{kT/\hbar\omega_A}$ with $\omega_A \approx 200$ cm^{-1}.

TABLE I. Lithium niobate phonon parameters (representative data fits).

T (K)	Soft-mode frequency (cm^{-1})	Damping[a] γ_0 (cm^{-1})	$\delta^2\tau$ (cm^{-1})	$1/\tau$ (cm^{-1})
		Stoichiometric sample		
297	279±12	13±6	225±60	uncertain
350	278±3	15±1	262±97	uncertain
656	266±18	37±26	286±136	uncertain
860	226±5	167±8	300±32	24±2
974	217±4	188±12	468±40	21±2
1083	228±5	224±1	632±10	19.6±0.2
1132	236±3	263±7	877±51	19±3
1172	237±5	317±15	1124±46	15.5±0.2
1224	229±11	452±35	1373±62	10.4±0.3
		Congruent sample		
297	275±8	11±4	uncertain	uncertain
474	267±2	19±1	uncertain	uncertain
612	249±2	58±1	251±1	7±10
787	240±0	122±8	uncertain	uncertain
848	226±4	132±6	426±43	17±1
974	220±3	169±7	458±28	18±1
1083	220±2	210±1	634±1	19±2
1171	229±4	259±10	1063±51	17±1
1224	232±2	366±1	1434±10	17±2

[a]The linewidth γ_0 (average for congruent and stoichiometric samples) satisfies $\gamma_0 = Ae^{kT/\hbar\omega_A}$ with $A = 6$ cm^{-1} and $\omega_A = 204$ $cm^{-1} \approx \omega_0$ over the temperature range 297 K $\leq T \leq$ 1224 K.

In Fig. 4 some similar spectra are shown for the stoichiometric specimen. The data are qualitatively similar. The main visual difference is the appearance of "leakthrough" spectral peaks at about 80 cm^{-1}; these are due to E-symmetry modes that appear in the zz spectra due to internal strain in the sample.[1] In addition, the quasielastic scattering becomes narrower in the stoichiometric sample than in the congruent one at the same temperature, for temperatures approaching T_C. Figure 5 plots the T dependence of $\tau\delta^2$ and τ^{-1} for the stoichiometric specimen; the dependence of $\tau\delta^2$ is virtually unchanged from the congruent values (these values are tabulated in Table I), but the values of τ^{-1}, while in the same range as those for the congruent specimen, are not independent of temperature. They change by a factor of 2 between 974 and 1224 K and extrapolate roughly to zero at $T_C = 1483 \pm 10$ K. Note in particular that $1/\tau$ at 1224 K for the stoichiometric sample is about half that for the congruent specimen, a difference outside the experimental uncertainty. A correlation submatrix for these parameters ω_0, γ_0, δ^2, and τ is shown in Table II.

It would be highly desirable to extend these measurements above 1300 K in order to see if this extrapolation is justified. At present our facilities do not permit measurements above 1225 K. However, based on the data in Fig. 5(b) we can say that there is a critical slowing down of the relaxation time τ as T approaches T_C from below (a line of zero slope through the data points falls well outside the experimental uncertainty) and that this effect is masked in
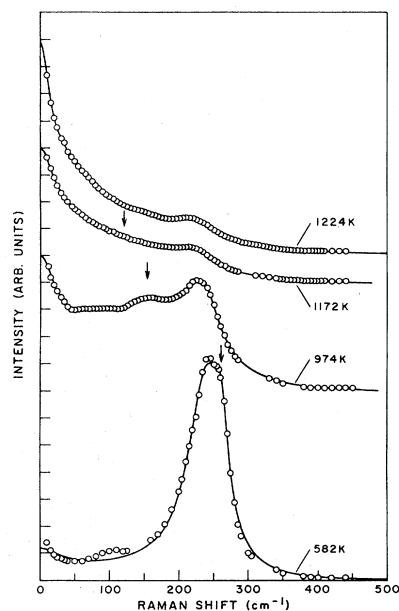

FIG. 4. Raman spectra of stoichiometric LiNbO$_3$. The four traces are for zz polarizability at 1224, 1172, 974, and 583 K. The weak feature in the 80—100 cm^{-1} region is scattering from E-symmetry modes due to internal strain in the sample. In contrast to the data shown in Fig. 2, the quasielastic scattering in this stoichiometric sample both increases in intensity and narrows as T approaches T_C from below.
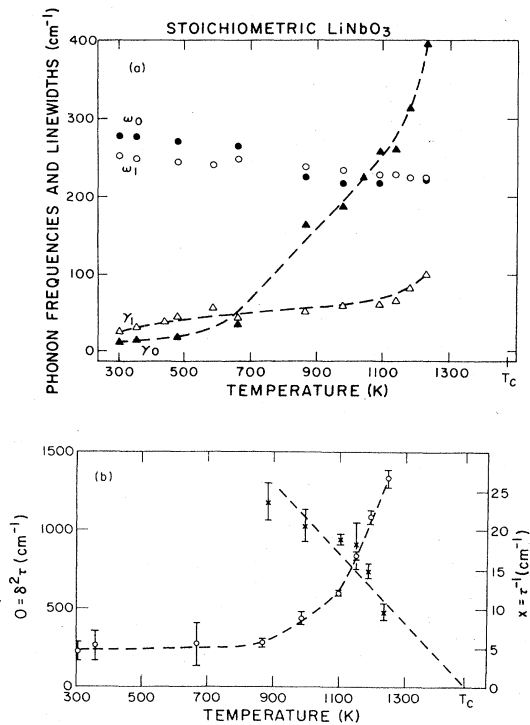
FIG. 5. (a) Temperature dependences of the fitting parameters for the spectra in Fig. 4. (b) Temperature dependences of the relaxation parameters for the spectra in Fig. 4. This stoichiometric sample shows an apparent temperature dependence of its relaxation time; the dashed line through the $1/\tau$ data points is a suggested mean-field critical slowing down. The solid curve through the $\tau\delta^2$ data is of the form $A(T_C-T)^{-1}$; the dashed curve is a guide to the eye. At low temperatures the values of $\tau^{-1}(T)$ are approximately the same for both congruent and stoichiometric samples, but at high temperatures $\tau^{-1}(T)$ for the stoichiometric specimen decreases to about half the congruent value. This decrease is outside the experimental fitting uncertainty.

the congruent specimen. A fit to the values of $\tau^{-1}(T)$ shown for the stoichiometric sample yields

$$\tau^{-1}(T)=\tau_0^{-1}(T_C-T)/T_C ,$$

with $\tau_0^{-1}=58\pm14$ cm^{-1}. This is the form, linear in reduced temperature, which might be expected in the mean-field approximation in a system in which critical slowing down of relaxation times occurs as a second-order phase-transition temperature is approached.

The T dependence of δ^2 is more accurate than that of $1/\tau$, discussed above. The data in Fig. 3(b) satisfy $\delta^2 \approx A(T_C-T)$, in agreement with the theory of Halperin and Varma[11] and in qualitative agreement with experiments on[12] RbCaF$_3$. As in Ref. 12, the T dependence of $\delta^2(T)$ is slightly faster than $(T_C-T)^{-1}$ and corresponds to an exponent of 1.4 ± 0.1, rather than unity. This is shown in Fig. 6, where a log-log plot of δ^2 vs
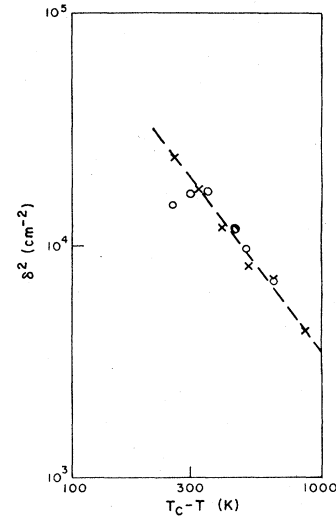

FIG. 6. Log-log plot of $\delta^2(T)=At^{-\gamma}$, yielding $\bar{\gamma}=1.4\pm0.1$. Circles are stoichiometric data; $\times$'s are congruent data.

$t=(T_C-T)/T_C$ for both congruent and stoichiometric samples gives an exponent $\bar{\gamma}=1.4$ in $\delta^2=At^{-\bar{\gamma}}$. However, the congruent sample data fit the assumed power law better than the stoichiometric data do; there is more scatter in the data for the latter.

IV. CONCLUSIONS

With increasing temperature LiNbO$_3$ exhibits a decrease in the peak frequency of its A_1-symmetry optical phonon at $q=0$ which has energy 274 cm^{-1} at room temperature. This is in accord with the original results of Johnston and Kaminow.[1] The absence of such a soft mode in the inelastic neutron scattering data of Ref. 2 is due to problems of intensity and resolution in that experiment[2] and unrelated to the question of displacive versus order-disorder dynamics. LiNbO$_3$ does not exhibit spectra typical of a displacive ferroelectric phase transition, however, in that the decrease in peak frequency of the soft

TABLE II. Representative correlation submatrices for fitting parameters for LiNbO$_3$ phonon spectra.

	ω_0	γ_0	$\delta^2\tau$	τ
Congruent specimen at 848 K				
ω_0	1.00	0.72	0.69	−0.04
γ_0	0.72	1.00	0.78	0.41
$\delta^2\tau$	0.69	0.78	1.00	0.06
τ	−0.04	0.41	0.06	1.00
Stoichiometric specimen at 1172 K				
ω_0	1.00	0.70	−0.28	−0.87
γ_0	0.70	1.00	0.47	−0.70
$\delta^2\tau$	−0.28	0.47	1.00	0.05
τ	−0.87	−0.70	0.05	1.00

mode arises almost entirely from rapidly increasing damping of the form $\gamma(T) \cong (6 \ \text{cm}^{-1}) e^{kT/\hbar\omega_0}$ rather than from decreases in the quasiharmonic frequency ω_0. In this respect $LiNbO_3$ resembles the order-disorder system[13] $Ag_{26}I_{18}W_4O_{16}$ rather than displacive systems such as $SrTiO_3$ or $LaAlO_3$.[14,15] It may be significant that ferroelectric $LiNbO_3$, $BaTiO_3$, and $PbTiO_3$ (Ref. 10) all have diverging linewidths for their soft modes, whereas nonferroelectric $LaAlO_3$ and $SrTiO_3$ do not.

The spectral distribution function at all temperatures quantitatively fits the prediction of that for a damped harmonic oscillator coupled to a Debye relaxation, with a relaxation time exhibiting critical slowing down for stoichiometric $LiNbO_3$ but a temperature-independent relaxation time for congruent specimens. The coupling constant $\delta^2(T)$ varies approximately as $(T_C - T)^{-1}$, in agreement with defect-theory predictions.[11] The microscopic mechanism of the relaxation process cannot be inferred from these studies; however, by comparison with[4] $LiTaO_3$, Li disorder is conjectured.

ACKNOWLEDGMENTS

*Permanent address: Oita University, Oita, Japan.

†Permanent address: Institute for Ceramics, Academy of Sciences, Shanghi, People's Republic of China.

[1]W. D. Johnston, Jr. and I. P. Kaminow, Phys. Rev. **168**, 1045 (1968); R. Claus, G. Borstel, E. Wiesendanger, and L. Steffan, Z. Naturforsch. **27A**, 1186 (1972).

[2]M. R. Chowdhury, G. E. Peckham, and D. H. Saunderson, J. Phys. C **11**, 1671 (1978); see also the related study of $LiTaO_3$. E. J. Samuelsen and A. P. Grande, Z. Phys. B **24**, 207 (1976).

[3]S. C. Abrahams and J. L. Bernstein, J. Phys. Chem. Solids **28**, 1685 (1967); S. C. Abrahams, W. C. Hamilton, and A. Sequeira, J. Phys. Chem. Solids **28**, 1693 (1967).

[4]M. E. Lines, Solid State Commun. **10**, 793 (1972).

[5]J. L. Servoin and F. Gervais, Solid State Commun. **31**, 387 (1979); A. F. Penna, S. P. S. Porto, and E. Wiener-Avnear, Solid State Commun. **23**, 377 (1977); and in *Proceedings of the 5th International Conference on Raman Spectroscopy*, edited by E. D. Schmid, J. Brandmuller, W. Kiefer, B. Schrader, and H. W. Schrotter (Schulz, Freiburg, 1976), p. 634; A. F. Penna, A. Chaves, and S. P. S. Porto, Solid State Commun. **19**, 491 (1976); and D. G. Bozinis, A. F. Penna, and S. P. S. Porto, in *Proceedings of the 5th International Conference on Raman*

Spectroscopy, edited by E. D. Schmid, J. Brandmuller, W. Kiefer, B. Schrader, and H. W. Schrotter (Schulz, Freiburg, 1976), p. 569.

[6]F. Schwabl, Phys. Rev. Lett. **28**, 500 (1972).

[7]S. M. Shapiro, J. D. Axe, G. Shirane, and T. Riste, Phys. Rev. B **6**, 4332 (1972); J. Feder, *Local Properties at Phase Transitions*, edited by K. A. Muller and A. Rigamonti (North-Holland, Amsterdam, 1976), p. 312.

[8]A. D. Bruce and R. A. Cowley, Adv. Phys. **29**, 219 (1980).

[9]J. F. Scott, Phys. Rev. Lett. **24**, 1107 (1970); J. Ruvalds and A. Zawadowski, *ibid.* **24**, 1111 (1970).

[10]G. Burns and B. A. Scott, Phys. Rev. Lett. **25**, 167 (1970); J. F. Scott, Proc. R. Soc. Edinburgh **70**, 25 (1971).

[11]B. I. Halperin and C. M. Varma, Phys. Rev. B **14**, 4030 (1976).

[12]R. Almairac, M. Rousseau, J.-Y. Gesland, J. Nouet, and B. Hennion, J. Phys. (Paris) **38**, 1429 (1977).

[13]F. Habbal, J. A. Zvirgzds, and J. F. Scott, J. Chem. Phys. **69**, 4984 (1978).

[14]P. A. Fleury, J. F. Scott, and J. M. Worlock, Phys. Rev. Lett. **21**, 16 (1968).

[15]J. F. Scott, Phys. Rev. **183**, 823 (1969).